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H. A. McTAGGART, M.A.

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The Electrification at Liquid-Gas Surfaces.

By H. A. M^c^Taggart, *M.A. Toronto*; *Research Student of Gonville and Caius College, Cambridge* *.

WHEN a liquid in the form of drops falls through a gas and splashes against an obstacle it is found to be electrified. At the same time the gas acquires a charge of the opposite sign. This charge found on the liquid varies with the liquid, the gas through which it falls, the nature of the obstacle on which it strikes, and the force of the impact. To account for this electrification it is usually supposed that at the surface of separation between the liquid and the gas, a double layer is formed, the two surfaces of which are oppositely charged, and that the shock mechanically pulls these charges apart. This separation of electrifications is found to be produced by almost any kind of mechanical disturbance acting at the surface if the forces in the disturbance act quickly enough (Becker, *Jahrb. d. Rad.* ix. p. 52, 1912). The breaking away of a drop of water from a dripping tap, the bubbling of a gas through the surface of water, or the blowing of water into spray, are accompanied by disturbances of this kind. Even the sudden separation of two wetted towels which have been pressed together, will charge the towels with one sign and the air with the opposite sign.

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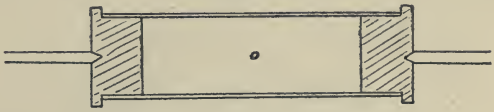
* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

The changes that can be produced in the electrification by mechanical means are modified by the nature of the gas in contact with the liquid and by dissolved salts or other impurities which it may contain. In experiments by Professor J. J. Thomson (Phil. Mag. xxxvii. p. 341, 1894) the action of the gas upon the electrification produced was shown to be considerable. For example, distilled water falling through air acquired a positive charge. When it fell through hydrogen it became negatively charged, while, if allowed to fall through its own vapour, it acquired no charge. Small quantities of salts dissolved in the water produced very remarkable effects on the electrification. The most active in this respect were some of the organic salts which are known to be readily adsorbed into the surface (Freundlich, *Kapillarch.* p. 248). This fact has suggested that the electrical double layer may be a result of adsorption.

It might be expected that the nature of this double layer, if it actually exists, would be influenced not only by the liquid and the salts dissolved in it, but to some extent also by the gas. At liquid-solid surfaces the electrification is not determined by the solution alone. The solid plays an important part—as experiments in cataphoresis and electric endosmose clearly show—but the way in which the solid (or gas) affects the charge in the double layer is not apparent. Nor is it clear how the ions of the dissolved salts, or those of the liquid itself, enter into the formation of the layer. To add to the information on these points is the object of this paper, which describes some experiments on liquid-gas surfaces.

In 1861 Quincke observed (Pogg. *Ann.* cxiii. p. 513, 1861) that in water through which an electric current was passing, small bubbles of air moved toward the anode, while in turpentine they moved toward the cathode. This motion must be due to the presence of an electric charge upon the surface of the bubble, and its velocity will then be a measure of the charge. An examination of these velocities will thus provide some further data regarding the electrification at liquid-gas surfaces. In his experiments Quincke used glass tubes of small bore (0·4 to 2 mm. diam.) in which to observe the motion of the bubbles. One disadvantage in such small tubes is the disturbing effect of the endosmose currents, besides which there is the difficulty of keeping the bubble from sticking to the wall. Instead of this it is possible to use a glass tube rotating about its axis as shown in fig. 1.

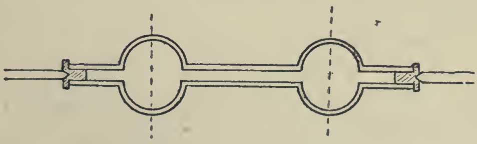
Fig. 1.



The ends are closed by metal electrodes which are countersunk to receive the pivot points upon which the tube rotates. When the tube is in motion the current is led in through the liquid by means of the pivot supports. A bubble of gas in the rotating liquid takes up a position on the axis if the bubble is fairly small and if the speed of rotation is high enough. The motion of the sphere of gas along the axis due to an applied electric field may then be examined. This is the method employed in this paper.

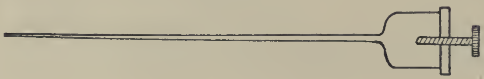
To reproduce the effects observed by Quincke a preliminary trial was made with a rotating cell of the form shown in fig. 2.

Fig. 2.



It consists of a piece of capillary tubing near the ends of which two bulbs are blown. The inner surface from the ends up to the dotted lines was silvered in order to provide electrodes as large as possible. A small hole was left in one of the bulbs through which a bubble of gas could be introduced. This could be done very easily when the tube was at rest by using a fine tube fitted with a screw as shown in fig. 3.

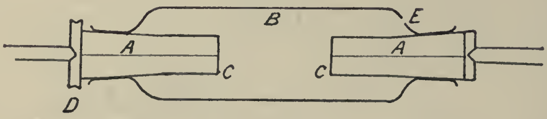
Fig. 3.



It is made by drawing down an ordinary piece of glass tubing to a fine capillary and fastening a plate with a screw through its centre to the large end. When this apparatus is filled with water, if the screw be turned back the water retreats along the capillary followed by air, any quantity of which may then be expelled into the cell by turning the screw forward again. The cell was set in motion by a small electric motor connected to it by a belt of fine thread running over pulleys. This apparatus gave, even when set up in a more or less careless way, a very interesting exhibition of the bubble moving along the axis, now fast, now slow, as the potential between the ends was altered.

The velocity of a bubble of gas in such a cell is not, however, its real velocity through the liquid. In tubes of such small bore the endosmose sets up a current along the wall which returns along the axis, increasing or diminishing the true velocity according to circumstances. Another error, due to currents in the liquid, is introduced if the speed of rotation is not uniform, an error which it is almost impossible to avoid with an ordinary type of motor. In making actual measurements a cell of the form shown in fig. 4 was used.

Fig. 4.



The glass stoppers AA with platinum electrodes on their ends *cc* are ground into the tube B and furnished with metal bearings to run on the pivot points. A wire running through the stoppers connects the electrodes with the bearings. Bubbles of gas are introduced through a small hole at E. To ensure uniform rotation a Rayleigh motor (Scientific Papers, Lord Rayleigh, vol. ii. art. 56, p. 355) was used which drove a belt of thread over the pulley D. This worked fairly well if the thread was kept moistened with oil to prevent it slipping. The drifting of the bubble due to gravity was controlled by levelling-screws in the base of the apparatus. It was found that when all adjustments were made, the bubble, observed through a low-power microscope, would remain on the hair-line for some time.

With this cell an examination was made of (1) the effect of the size of the bubble on its velocity, (2) the relation between the velocity and the potential gradient, (3) the value of the velocity in distilled water of conductivity about 5.10^{-6}. The velocity was measured by noting the time—with a stop-watch—taken by the bubble to move over a fixed number of scale-divisions in the microscope. By a simple device the watch was started (or stopped) and the electric field applied (or removed) simultaneously. To eliminate a possible error due to the tube not being exactly level, the bubble was made to move a definite distance in one direction and to retrace it in the opposite direction. The diameter of the bubble was measured on the microscope-scale as the tube was rotating. The following readings on bubbles of air of various sizes show the accuracy obtained. In the first column is the diameter in mm.; in the second, five successive readings of the time required to move over 20 scale-divisions (45 divisions $=1$ mm.). Since the field between the electrodes was not uniform, the readings were taken at a fixed distance from one electrode.

Diam.	Time in secs.					Average.
·06	$9\frac{1}{2}$,	$10\frac{1}{2}$,	$10\frac{1}{2}$,			10·1
·08	10 ,	$10\frac{1}{2}$,	$10\frac{1}{4}$,	$10\frac{3}{4}$,	$9\frac{3}{4}$	10·2
·10	10 ,	$10\frac{1}{4}$,	$10\frac{1}{4}$,	$10\frac{1}{2}$,	$10\frac{3}{4}$	10·3
·12	$10\frac{3}{4}$,	$10\frac{1}{4}$,	$10\frac{1}{4}$,	$10\frac{1}{2}$,	11	10·5
·14	10 ,	10 ,	10 ,	$10\frac{1}{4}$,	10	10·0
·16	10 ,	10 ,	10 ,	10 ,	10	10·0
·16	$10\frac{3}{4}$,	11 ,	11 ,	11 ,	$10\frac{3}{4}$	10·9

If the difficulty of maintaining a uniform speed of rotation were fully overcome, the average time for bubbles of different sizes would probably be the same. Bubbles larger than ·2 mm. gave inconsistent results, due apparently to eddy currents set up by their failure to remain exactly on the axis. Very small bubbles, formed sometimes by the gradual absorption of the gas by the water, were observed to leave the axis in an irregular way as if their buoyancy were no longer sufficient to keep them on the axis. It may be concluded then, that, within the limits given in the table above, the velocity is independent of the size.

The velocity is proportional to the potential gradient, at least for differences of potential that are not very small. Measurements of velocities in fields of less than 6 volts per cm. were not made. The following table gives the time taken by a bubble in moving 40 divisions under a field of 16 volts and of 8 volts. Readings were taken at six points equally spaced between the electrodes to observe at the same time the variation in the field. Near the electrodes the times are shortest, *i. e.* the velocity is greatest.

	1.	2.	3.	4.	5.	6.
16 volts	$8\frac{1}{4}$	$10\frac{3}{4}$	12	$11\frac{1}{2}$	$10\frac{1}{4}$	$8\frac{3}{4}$
	$8\frac{1}{2}$	10	$11\frac{3}{4}$	12	$10\frac{1}{2}$	$8\frac{1}{2}$
Average	8·3	10·3	11·8	11·7	10·3	8·6
8 volts	18	21	25	26	24	20
	16	20	23	23	$20\frac{3}{4}$	17
Average	17	20·5	24	24·5	22·3	18·5

When the voltage is doubled the time is halved, *i. e.* the velocity is doubled.

To get an estimate of the actual velocity per unit fall of potential, it is necessary to know the average value of the velocity. This may be got by plotting a curve with the distances of a point on the axis from the electrode as abscissæ, and as ordinates the velocities or times to move over a given distance about the point, and finding the average ordinate for the curve. The value obtained for one set of readings was 9·4 sec. which was the average time taken to move 20 divisions of the scale each way or 40 in all. The fall of potential was 22·8 volts per cm. This gives a velocity in cm./sec./volt/cm. of

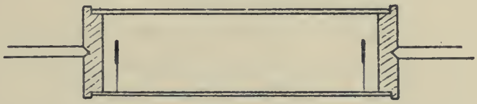
$$\frac{40}{45 \cdot 10} \cdot \frac{1}{9 \cdot 4} \cdot \frac{1}{22 \cdot 8} = 4 \cdot 1 \, . \, 10^{-4}.$$

An average of four sets of readings at another time gave $3 \cdot 9 \, . \, 10^{-4}$. It may be concluded then that the velocity of small spheres of air in water of this purity is about $4 \, . \, 10^{-4}$ cm./sec./volt/cm.

No effort was made to prepare water of extreme purity, but rather to obtain by a fixed method of distillation water of fairly constant quality. It invariably contained air and carbon dioxide, to some extent. Under these conditions spheres of hydrogen, oxygen, and illuminating gas all had practically the same velocity as air. For hydrogen an average of three sets of readings gave $4\cdot2 \,.\, 10^{-4}$; of three others $4\cdot1 \,.\, 10^{-4}$. From Professor Thomson's experiments on the electrification of drops one might expect to find a difference in the velocity of hydrogen and oxygen. In his experiments the water was carefully freed from dissolved gases and a perfectly fresh surface was exposed with each drop, conditions difficult to obtain in a rotating cell. However, water thoroughly boiled was tried but no change of sign occurred with hydrogen as compared with oxygen, and, as far as could be observed, there was no difference in velocity. No actual measurements were made on account of the rapidity with which the bubble was absorbed by the water.

Experiments were then made to study the influence of small amounts of dissolved electrolytes upon the surface electrification. For this purpose a slightly different form of cell was used, designed to allow the use of larger currents than were possible in the last cell. A straight piece of glass tubing 2·3 cm. in diameter and about 7 cm. long was fitted with brass stoppers covered on one face with platinum to act as electrodes (fig. 5).

Fig. 5.



Two thin disks of glass mounted just in front of the electrodes prevented small bubbles of gas which might form on these from drifting out into the liquid and disturbing the bubble under observation. For the very dilute solutions that were used this cell was found to be fairly suitable. It was filled and emptied through a small hole in the end. Mathematically (Lamb, Brit. Assoc. Report, 1887, p. 495), in such a closed cylinder the endosmose along the walls would set up a return current along the axis. In a tube of this size, however, it would be negligible, giving an error of the same order as that present in U-tube methods of determining the velocities of colloidal suspensions.

A considerable amount of work has been done on liquid-solid surfaces and on the effects of dissolved electrolytes on the surface electrification. Hardy (Journ. Phys. Chem. iv. p. 235, 1900) gives as a general rule that, in the case of colloids, the coagulative power of a salt is determined by the valency of one of its ions. That ion which is of the opposite electrical sign to the colloidal particle is the one which causes the coagulation, *i. e.* it is the ion which annuls the charge on the colloid. In endosmose experiments with porous diaphragms, Perrin (*Journ. de Chim. & Phys.* ii. 1904, iii. 1905) finds a similar rule to hold regarding the activity of an ion in discharging the solid-liquid surface. A trivalent ion is much more active in this respect than a monovalent ion. A positive ion reduces the charge on a negatively charged surface and conversely. In general, at a liquid-solid surface, the solid is charged negatively in a basic solution, and positively in an acid solution. It will be seen that these rules apply, in a general way, to liquid-gas surfaces as well.

The two acids HCl and HNO_3, having the monovalent positively charged hydrogen ion, were tried in very dilute solutions. With increasing concentration the negative charge on a bubble of air was reduced until it was practically neutralized. Very strong solutions could not be used because of the disturbing effect of gases given off at the electrodes. In the highest concentration that was used, however, no reversal of the sign was found. HCl was used in concentrations from 10^{-7} equivalents per c.c. to 10^{-5} equivalents per c.c. as estimated against standard baryta-water. HNO_3 over a similar range of concentrations gave practically the same results as HCl.

To obtain, if possible, some examples of a reversal of the sign of the charge, a number of trivalent positive ions were chosen. Readings for three nitrates are given in the tables below. In the first column are the concentrations in equivalents per c.c., in the second the time taken by a bubble of air in moving over a fixed distance, and in the third the sign of its charge. When the velocities are too slow to be timed conveniently the words "slow," "faster," are used to give a general idea of the motion.

$La(NO_3)_3\,6\,H_2O$.	Time.	Charge.
	Seconds.	
$10^{-9}\,.\,7{\cdot}5$	40	−
$10^{-8}\,.\,7{\cdot}5$	64	−
$10^{-7}\,.\,3{\cdot}7$	240	−
$10^{-7}\,.\,7{\cdot}5$	—	0
$10^{-6}\,.\,3{\cdot}7$	slow	+

$Al(NO_3)_3 16 H_2O$.	Time.	Charge.
	Seconds.	
$10^{-9} . 4$	40	−
$10^{-9} . 8$	67	−
$10^{-8} . 2{\cdot}4$	slow	+
$10^{-8} . 4$	,,	+
$10^{-7} . 4$	faster	+
$10^{-6} . 2$	,,	+

$Cr(NO_3)_3 18 H_2O$.	Time.	Charge.
	Seconds.	
$10^{-9} . 4$	20	−
$10^{-8} . 2$	28	−
$10^{-8} . 4$	34	−
$10^{-7} . 1{\cdot}2$	50	−
$10^{-7} . 4$	80	−
$10^{-7} . 8$	slow	−

The first two salts reverse the sign of the charge on a water-air surface, and it seems likely that the chromium salt would have done the same if the concentration could have been made a little greater.

The following tetravalent nitrates were then tried :—

$Th(NO_3)_4 12 H_2O$.	Time.	Charge.
	Seconds.	
$10^{-11} . 7$	26	−
$10^{-10} . 7$	77	+
$10^{-9} . 7$	57	+
$10^{-8} . 1{\cdot}4$	48	+
$10^{-8} . 2{\cdot}8$	40	+

$Zr(NO_3)_4$.	Time.	Charge.
	Seconds.	
$10^{-9}.5$	23	–
10^{-8}	–	0
$10^{-8}.5$	95	+
10^{-7}	35	+
$10^{-7}.5$	30	+

The positive ions Th and Zr not only neutralize the negative charge but they give the surface a large positive charge. The thorium salt is the most remarkably active in this respect of all the salts used.

Two tetravalent chlorides were tried but they showed very slight effects :—

$PtCl_4\ 5\ H_2O$.	Time.	Charge.
	Seconds.	
10^{-9}	16	–
10^{-7}	17	–
10^{-6}	26	–
$10^{-6}.2$	40	–

$SnCl_4\ 8\ H_2O$.	Time.	Charge.
	Seconds.	
$10^{-9}.7$	19	–
$10^{-8}.3{\cdot}5$	28	–
$10^{-8}.7$	32	–
$10^{-7}.1{\cdot}4$	25	–

In these cases it is likely that the metal forms part of a complex ion, and is therefore not free to exhibit the full effect of its valency (Whetham, 'Theory of Solutions,' p. 196).

Hexavalent chromium in CrO_3 gave results of a similar kind :—

CrO_3.	Time.	Charge.
	Seconds.	
10^{-8}	20	–
10^{-7}	25	–
$10^{-7}.5$	30	–
10^{-6}	50	–
$10^{-6}.2$	?	–

The effect of negative ions on positively charged bubbles was then examined. For this purpose the trivalent and tetravalent ion ($FeCy_6$) in potassium ferri- and ferrocyanide were used. To obtain a positively charged bubble to begin with, a solution containing 10^{-8} equivs./cc. of thorium nitrate was made. In this a bubble of air has a small positive charge. The following tables show the effect on this positive charge of the negative ions in different concentrations.

K_3FeCy_6.	Time.	Charge.
	Seconds.	
0	slow	+
10^{-8}	,,	+
$10^{-8}.5$	,,	almost zero.
10^{-7}	—	0
$10^{-7}.2$	slow	–
$10^{-7}.3$	40	–

$K_4FeCy_6\,3H_2O$.	Time.	Charge.
	Seconds.	
0	slow	+
$10^{-9}.2$	,,	+
$10^{-9}.4$	43	–
$10^{-9}.8$	30	–
10^{-8}	20	–
$10^{-8}.3$	28	–
10^{-7}	37	–

The tetravalent salt neutralizes the positive charge at a much smaller concentration than the trivalent.

The monovalent positive ion H, and negative ion OH in HCl and KOH respectively were tried in water made electrically neutral by adding a very small quantity of $Al(NO_3)_3$. When HCl was added to this solution the bubble became positively charged. When KOH was added it gave the bubble a negative charge.

In ordinary distilled water bubbles of hydrogen and oxygen have practically the same velocity. There is probably a difference which, however, cannot be detected with certainty under the conditions of the experiment. This difference might show itself more definitely in a solution almost electrically neutral. The following readings with air, hydrogen, and oxygen were taken to see if a difference could be observed :—

$Al_2(SO_4)_3$.	Air.	O.	H.
$10^{-9}.2$	−	−	−
$10^{-9}.3$	0	−	+
$10^{-9}.5$	+	−	+
10^{-8}	+	0	+
10^{-7}	+	+	+

It appears that the hydrogen changes sign at a smaller concentration than the oxygen, so that in this case, at least, the surface electrification is not independent of the gas.

The following unexpected effect was observed when water was used which had been boiled to free it from air. The water was made almost but not quite electrically neutral by adding $Th(NO_3)_4$, and a bubble, placed in this solution, was observed under the microscope. In this partially air-free solution, the bubble was gradually absorbed by the liquid and finally disappeared, but its electric charge during this process did not remain the same. At first it was negatively charged. As it diminished in size the negative charge gradually disappeared until the bubble was neutral. As it continued to diminish in size it began to acquire a positive charge which slowly increased till the bubble became too small to examine. This effect will be referred to again.

Discussion.

Small spheres of gas electrically charged in water move in an electric field with a velocity of the same order as the velocity of colloidal particles. The motion of these particles is regarded as due to a continuous relative displacement in opposite directions of the two faces of a double layer, one of which is fixed to the solid particle. The velocity of such a particle is given by Lamb's formula (B. A. Report, p. 495, 1887)

$$u = \frac{\mathrm{H}\rho\delta}{\mu},$$

where u = vel. of particle, ρ = surf. density of charge,
H = pot. grad., δ = thickness of layer,
μ = viscosity of liquid.

This equation will apply to the motion of spheres of gas in a liquid if a double layer exists at the liquid-gas interface. That surface of the double layer which touches the gas would not be attached to a solid surface as in the case of a colloidal particle, but it might be regarded as forming a sort of flexible shell filled with the gas.

There is no doubt that a film of some rigidity is formed about the gas, which acts toward the contiguous liquid like a solid surface so far as endosmose effects are concerned. Hardy (Proc. Roy. Soc. B. lxxxiv. 1911) has examined with some care the case of a plane air-water surface. An electric current was observed to drive small particles of graphite immersed just under the film past the surface with the same velocity as particles near the solid walls of the containing vessel. Small particles resting upon the film did not move appreciably. A sphere of gas in liquid is enclosed in a film of this sort which forms one surface of the double layer and preserves its identity, more or less, as it moves through the liquid. We may, then, with some reason assume Lamb's formula to be applicable and employ it to find the charge on a bubble of air in water.

We have in E.S. units :—

$$\rho = \frac{\mu u}{\mathrm{H}\delta}$$

$$= \frac{0{\cdot}01 \,.\, 4 \,.\, 10^{-4}}{\frac{1}{300} \,.\, 10^{-8}},$$

putting the viscosity at 0·01 and the thickness at 10^{-8} cm., or

$$= \frac{0{\cdot}01 \,.\, 4 . 10^{-4}}{\frac{1}{300} \,.\, 10^{-8} \,.\, 3 \,.\, 10^{9}} \text{ coulombs}$$

$$= 4 \,.\, 10^{-5} \text{ nearly.}$$

The charge on a sphere of any size may be found by multiplying this density by the surface area. The following table compares with this the amount of electrification set free (1) by a drop in a waterfall experiment, (2) by a drop broken up in a current of air (Simpson, Phil. Trans. A. 209. p. 379, 1909), and (3) by the breaking off of a drop from a source (see Becker, *loc. cit.*).

Experiment.	Diam. of sphere.	Charge calc. in coulombs.
Cataphoresis	7·8 mm.	$7{\cdot}6 . 10^{-5}$
	4·4 „	$2{\cdot}4 . 10^{-5}$
Waterfall exp.	7·8 „	$2{\cdot}8 . 10^{-12}$
	4·4 „	$0{\cdot}89 . 10^{-12}$
Drops broken up by a current of air	7·8 „	$1{\cdot}7 . 10^{-12}$
Breaking off of a drop...	4·4 „	$5{\cdot}28 . 10^{-14}$

If the estimates made in these various cases are not too wide of the mark, it is evident that only a very small fraction of the charge is set free by such mechanical disturbances as those mentioned.

The difference of potential (V) between the surfaces of the double layer may be calculated from

$$\frac{\mu u}{\mathrm{H}\delta} = \rho = \frac{\mathrm{KV}}{4\pi\delta}, \quad i.e. \quad \mathrm{V} = \frac{4\pi\mu u}{\mathrm{HK}},$$

if the thickness of the layer be small in comparison with the radius of the sphere.

In E.S. units

$$\mathrm{V} = \frac{4 . 3{\cdot}14 . 0{\cdot}01 . 4 . 10^{-4}}{\frac{1}{300} . 81},$$

or in volts

$$= \frac{4 . 3{\cdot}14 . 0{\cdot}01 . 4 . 10^{-4} . 300}{\frac{1}{300} . 81},$$

$$= \underline{0{\cdot}055.}$$

In a consideration of the electrical effects observed at liquid-gas surfaces, differences must be noted between the conditions of experiments like waterfall experiments, bubbling of gas through water, or spraying experiments and cataphoresis experiments like those described in this paper. The surface-density of electrification need not be the same in the two cases. In solutions the concentration of the salt in the surface does not reach an equilibrium value the moment the surface is formed. For this reason, the electric density will have a value in a freshly formed surface different from its value in an older surface. One may refer to the two types of experiment as the dynamical and statical, in the same way that one refers to corresponding methods of measuring surface-tensions of solutions. Not only is there a gradual adsorption of salt into the surface on the liquid side, but there may be an adsorption of gas on the opposite side. In a dynamical experiment the surface will not be in that equilibrium state which exists in a statical one.

Again, it is possible that the gas does not play the same part in producing the electrification in the two cases. For example, it is not improbable that a sphere of water-vapour in water would be found to be charged in the statical experiment, while a drop of water falling through its own vapour is known to give no electrical effect. In the static case H and O show very slight differences in charge, but in dynamic experiments they give rise to charges of opposite sign. The fact that so many substances in contact with water are negatively charged indicates that water by itself produces an electrification upon which is superposed an electrification due to the substance in contact with it. It is probable that in the static experiment the hydrogen and oxygen exert a very small influence on the charge observed, but in dynamic experiments they play an important part. When these gases are torn away from the water by the mechanical forces, the violence of the separation may give rise to an electrification which is not apparent in the statical observations and which depends as to its sign and amount upon the nature of the gas.

The changes in the electrification produced by dissolved salts are nct easy to explain, the difficulty being increased by a lack of knowledge of the nature of the ions formed and the amount of hydrolysis which occurs. Where there is complete dissociation—as in the dilute solutions here used—the ions formed would tend to charge the surface with their own sign. This tendency, however, is stronger in some ions than in others, and the same ion does not exhibit the same power to charge different surfaces. The H-ion, for example, shows quite different powers of precipitation toward colloidal As_2S_3, gold-sol, mastic and egg-white (Mines, *Koll.-Chem. Beih.* iii. p. 193, 1911–12). In the case of liquid-gas surfaces the H-ion does not seem to show a very strong charging power, as indicated by the acids HCl and HNO_3.

Of the three trivalent nitrates of La, Al, Cr, the first shows scarcely any hydrolysis (Perrin, *loc. cit.*), and one might expect the effects observed to be due to the simple ions La and NO_3. In the other two cases hydrolysis produce a supply of H-ions, to which the higher activity of the Al-salt may be ascribed. One would expect the Cr-salt for the same reason to be more active than La, but its effect is even less. Similar discrepancies occur in the stability of these metals in colloidal form (Biltz, *Berl. Ber.* xxxv. p. 4434), and no satisfactory explanation seems possible at present.

Of the two tetravalent nitrates Th and Zr the first is unusually active, the merest trace of the salt being sufficient to reverse the charge. Both salts hydrolyse and their colloidal hydroxides are prepared by dialysis. Thorium is remarkable also for its stability as a colloid, being much more stable in the presence of added electrolytes than Zr (Biltz, *loc. cit.*). In endosmose experiments using water against glass and quartz, Elissafoff (*Zeit. Phys. Chem.* lxxix. p. 385, 1912) finds that $Th(NO_3)_4$ has the same high charging power. This activity cannot be due to the presence of H-ions resulting from hydrolysis altogether, because the conductivity of the solution is relatively small. It has a large atomic weight, a fact worth noting in connexion with similar observations on the activity of heavy metals in endosmose experiments.

The chlorides of platinum and tin and the oxide of chromium evidently produce ions whose charges are small. Simple ions are not formed in these cases—a necessary condition apparently for the production of the greatest effect on the surface electrification.

The two negative ions, $FeCy_6^{\cdots}$ and $FeCy_6^{\cdots\cdot}$, follow the valency rule that the ion with a larger charge is more active than one with a smaller charge. Similar results for positively charged copper in colloidal solution have been obtained by Burton (Phil. Mag. vol. xvii. no. 100, April 1909) who found the charge to be reversed by K_3PO_4 and $K_3(FeCy_6)$.

In a general way the valency determines the charging power of an ion, but it is not the only factor apparently which has an influence. The greater activity of the ions of the heavy metals has been mentioned. The complexity of the ion also is associated with peculiarities in its activity. Mines (*loc. cit.*) has examined the action on colloidal substances of the complex trivalent ion $[Co(NH_3)_6]$ in Luteo-cobalt chloride and of simple trivalent ions. Some colloids are sensitive to both complex and simple ions, and some only to simple ones. An emulsion of olive-oil in water differentiates between the two, the simple ion being 170 times more powerful in precipitating the oil.

From these experiments with a rotating cell, it would seem that in the static type of experiment the charge at a water-gas surface is very slightly affected by the nature of the gas. Let us suppose for simplicity that the gas has no effect and that—following Prof. J. J. Thomson's view—the liquid in the surface layer is chemically unsaturated. The adsorbed gas, oxygen or hydrogen for example, would become attached to water molecules, but in such a way as not to affect the value of the charge in the electrical double layer, which would have the same sign and value as if the gas were absent. When, as in a waterfall experiment, a separation of the gas and water molecules occurs, the electrons are shared between them in a different way. Oxygen, having an affinity for negative electrons, will carry away an excess of them, giving the gas a negative charge. Hydrogen will leave an electron behind in the water and go off positively charged. In other words, the dynamical experiment brings out the difference in the chemical, *i.e.* the electrical, nature of the gas.

This simple view may be slightly modified in an actual case. Oxygen might attract negative ions into the surface and give it a larger negative charge than hydrogen would, as is shown, for example, in the comparison readings for these two gases in $Al_2(SO_4)_3$. In the static experiments the ions in the liquid will determine the surface charge, and since in water a surface is always negative, one may suppose the existence of a selective adsorption of $\overset{-}{\mathrm{O}}\mathrm{H}$ ions. In support of this is the fact that the surface is electrically neutral when $\overset{+}{\mathrm{H}}$ ions are in excess, as in acid solutions (leaving polyvalent ions out of consideration). When dissolved salts are present, their adsorption modifies the charge again, but the gas in contact still shows scarcely any effect. This neutrality was observed by Metcalf (*Zeit. Phys. Chem.* lii. p. 1, 1905) on the formation of films or crusts upon water by methyl violet, peptone, &c. He could detect no difference in the films when oxygen or hydrogen was in contact with them. A similar behaviour is observed in the change of sign which occurs when a bubble of hydrogen or oxygen is slowly absorbed into a solution of thorium nitrate as described above. When first introduced into the liquid the bubble is negatively charged. As it diminishes in size it gradually becomes neutral and then slowly takes on a positive charge. The effects are exactly those that would be produced if the concentration of the salt were slowly increased, as shown in the table above for thorium nitrate. It is natural to conclude that a progressive change in the concentration at the surface takes place as the bubble gets smaller. The surface layer first formed adsorbs a certain amount of salt which it apparently retains as it gets smaller, thus increasing the concentration. As in Metcalf's experiments no difference could be observed between the action of hydrogen and oxygen in this case.

This view of the action of the gas in these experiments is merely an hypothesis, and the work is being continued with the object of finding out more accurately the part played by the gas and by the salts dissolved in the liquid.

Summary.

A rotating cell method of examining the electric charge on small spheres of gas in a liquid has been worked out.

Quincke's observations on the movement to the positive pole of small spheres of air, oxygen, and hydrogen in distilled water were repeated, using the rotating cell.

The velocity of small spheres of gas in water was found to be proportional to the potential gradient and independent of their size (within limits).

The velocity of spheres of air, oxygen, and hydrogen in water was found to be about $4 \cdot 10^{-4}$ cm./sec./volt/cm.

Dissolved salts affect the charge at a gas-liquid surface, the activity of the salt depending on the charge carried by its ions in solution.

An air-water surface—in the absence of polyvalent ions—is electrically neutral in a slightly acid solution.

A sphere of gas in a solution can change the sign of its charge as it diminishes in size, by being absorbed into the solution.

Under the conditions of these experiments the electric charge at a liquid-gas surface appears to be almost independent of the nature of the gas.

My best thanks are due to Professor Sir J. J. Thomson for suggesting this research and for his kind advice during the progress of the work.

From the PHILOSOPHICAL MAGAZINE, vol. xxviii. *September* 1914.

Electrification at Liquid Gas-Surfaces. *By* H. A. McTAGGART, *M.A., Toronto ; Research Student of Gonville and Caius College, Cambridge*[*].

IN a previous paper (Phil. Mag. Feb. 1914, p. 297), the velocity of small bubbles of air, hydrogen, and oxygen in distilled water subject to a fall of potential was examined and found to be about 4.10^{-4} cm./sec./volt./cm. This corresponds—on the assumption of an electric double layer—to a density of electrification over the surface of the bubble of 4.10^{-5} coulomb approximately. In the same paper it was shown that the surface charge may be varied by the presence in solution of minute quantities of some inorganic salts and acids. The salts which are most effective in altering the surface charge are these containing ions of large valency. In some way not clearly understood, these ions enter the surface layer and make their presence evident in the charge they impart to it. There is a kind of selective adsorption in liquid-gas surfaces—an adsorption which also plays a part in the cataphoresis of solid and liquid particles.

The degree of adsorption of a dissolved substance is connected—qualitatively—with the change in the surface tension by the well-known formula :—

$$u=-\frac{c}{\mathrm{RT}}\frac{d\sigma}{dc},$$

where u = excess of salt in unit area of surface,
σ = surface tension,
c = concentration of salt in the liquid.

This equation expresses the fact that substances which lower the surface tension are present in the surface layer in excess, while substances which raise the surface tension are present in smaller concentration in the surface than in the body of the liquid. To the first class belong a number of organic compounds amongst which are the simpler alcohols and fatty acids, to the second belong many inorganic salts. The characteristic action of small concentrations of these two classes of substances on the surface tension of water is expressed in the law of Gibbs :—"a small amount of dissolved substance may lower the surface tension very much ; a small amount can never raise it very much." In the case of aqueous solutions of the alcohols and fatty acids—which are known to lower the surface tension very rapidly—the surface layers will be relatively rich in these substances and this will be even more the case in very dilute solutions. It is to be expected that solutions of this class would in cataphoresis experiments show effects depending upon this property.

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[*] Communicated by Sir J. J. Thomson, O.M., F.R.S.

In this paper the velocity of bubbles of air has been examined in aqueous solutions of a number of alcohols, fatty acids, &c., and in a few pure alcohols. The materials were Kahlbaum's—in some cases redistilled—and the water used was twice distilled, as explained in the last paper. The form of rotating cell was the same as that previously described. The results for solutions of the alcohols will be given first.

In solutions of methyl alcohol it was soon found that the velocity of a bubble of air depended upon its size,—an effect which is not observed in pure water. If the solution is not quite saturated with air, a bubble placed in it is gradually absorbed, diminishing slowly in size till it vanishes. During this process the velocity under a given fall of potential does not remain constant as it does in pure water but varies in a manner shown in the tables here given. The "time" here and elsewhere in the paper is the time taken by a sphere of air to move over 1 mm. and back again, *i. e.*, a distance of 2 mm.

4 per cent. sol. CH_3OH.

Diam. of bubble.	Time.	Volts/cm.
·2 mm.	28 secs.	98
·14	32	
·12	36	
·08	34	
·06	21	
·04	13	
·02	5	

1 per cent. sol. C_2H_5OH.

Diam. of bubble.	Time.	Volts/cm.
·14 mm.	23 secs.	38
·10	20	
·08	17	
·04	14	
·02	10	

Two examples only are given, selected from a large number. In nearly every such case the velocity increased as the size of the bubble diminished, approximating more and more closely to the velocity it would have in the distilled water used in the solution. The difference in velocity may be considerable, and it is at once evident what large errors may be introduced into such experiments on the cataphoresis of gas bubbles by the presence of any contamination having a large effect on the surface tension.

In a study of the action of these organic substances on the electrification of liquid-gas surfaces this disturbing effect must be dealt with at the same time. The way in which readings were taken is illustrated in the following table for methyl alcohol. The solutions were not quite saturated with air, so that a bubble, after being placed in the liquid, gradually became absorbed. The concentrations are measured by volume.

In all the cases mentioned in this paper the charge was of the same sign as in pure water, except, of course, when it was zero.

Methyl alcohol and water.

Concentrations.	Diam. of bubble.	Time.	Volts/cm.
1/4 alcohol (25 per cent.)...	·10 ·04	28 secs. 21	35
1/8 ,, ...	·14 ·10 ·04	21 17 14	
1/16 ,, ...	·14 ·12 ·10 ·08	19 15 14 11	
1/32 ,, ...	·14 ·12 ·10 ·06	16 14 12 11	
1/64 ,, ...	·14 ·12 ·08 ·06 ·04	19 16 15 12 11	
Dist. water	...	10	

The successive solutions were made by removing each time half the liquid in the cell and replacing it with the distilled water used. This method was found to give more consistent results than could be got by mixing each solution separately, though the concentrations are not so evenly distributed. In any case it is extremely difficult to get regular results showing the effect of the concentration of the alcohol on the velocity, *i. e.*, on the charge. From this list the times for bubbles of the same size, as nearly as possible,—(·1 mm.)—are selected and plotted in a curve against the concentration. This method will show at least the general shape of the curve. A similar series of readings was taken for each alcohol, and the selected lists are given all for bubbles as near the same size as possible. In every case the bubble carried the same sign of charge—negative—as it would in pure water.

Ethyl alcohol and water.

Conc.	Diam.	Time.	Volts/cm.
1/4 alcohol	·10	42 secs.	35
1/8 "		21	
1/16 "		15	
1/32 "		17	
1/64 "		15	
1/128 "		13	
1/256 "		16	
1/512 "		16	
0 "		11	

In this table the times do not decrease uniformly—an irregularity possibly due to the difficulty in keeping the pipette used for making the bubbles free from contamination.

Propyl alcohol and water.

Conc.	Diam.	Time.	Volts/cm.
1/4 alcohol	·10	No motion.	35
1/8 "		28 secs.	
1/16 "		20	
1/32 "		17	
1/64 "		15	
1/128 "		15	
1/256 "		16	
1/512 "		16	
1/1024 "		14	
Water		11	

In solutions containing 25 per cent. or more of this alcohol, no motion of an air-bubble could be observed under potentials as high as 130 volts/cm. In one experiment, however, with a 25 per cent. solution from which the excess of dissolved gas had not been all removed, a number of very small spheres —presumably of dissolved gas—collected on the axis of the cell near the bubble under examination. These were observed to move quite easily under 130 volts/cm., while the air-bubble remained stationary. Out of curiosity small spheres of benzine were tried in the same solution. These were found to move while a bubble of air did not.

The first three alcohols are miscible in all proportions with water. Isobutyl alcohol is not, but dissolves in about 12 parts of water. In this case a saturated solution was made to begin with, and readings were taken as in the other cases. The conductivity of this solution was three times that of water.

Isobutyl alcohol and water.

Conc.	Diam.	Time.	Volts/cm.	Time at smallest size.
Sat. soln. (8 %?)...	·10	?	35	
1/2 sat.		68 secs.		19 secs.
1/4 „		37		16
1/8 „		24		23
1/16 „		27		16
1/32 „		21		12
1/64 „		21		12
1/128 „		19		11

The variation of velocity with the size was even more marked in this case, and another column is given showing the times when the bubble was at its smallest just before vanishing as nearly as possible. The third reading in this column is probably an accidental error.

When more alcohol is added to the water than it will dissolve two phases are formed—a heavier, rich in water, for which readings are given above; and a lighter, rich in alcohol. In the former a bubble of air will move if it is small enough. In the latter it could not be observed to move under as much as 130 volts/cm. The conductivity of this solution was less than $\frac{1}{5}$ that of water.

The velocity of a sphere of the lighter phase in the heavier was observed. In this case also the heavier phase may not be quite saturated with the lighter, and it is possible to begin with a fairly large sphere and record its velocity for different sizes till it disappears. Readings for such a case are given here to show the effect.

Diam.	Time.	Volts/cm.
·36	22 secs.	40
·24	13½	
·18	9½	
·14	7	
·08	5	
·02	20	

It is interesting to observe a sphere so large as ·36 mm. in motion. It leaves a trail of liquid behind it of a concentration between itself and the rest of the liquid. As the size diminishes the velocity increases to a value larger than that found in any other case. At the smallest size, however, the velocity becomes slow again always—as if a residue of some kind remained to the last before dissolving.

Readings were also taken for amyl alcohol and water.

Amyl alcohol and water.

Conc.	Diam.	Time.	Volts/cm.
Sat. soln.	·10	15 secs.	35
1/2 sat.		17	
1/4 "		14	
1/8 "		12	
1/16 "		11	
1/32 "		10½	
1/64 "		11	
1/128 "		10	

The following readings were taken with a sphere of amyl alcohol placed in pure water and allowed to dissolve :—

Diam.	Time.	Volts/cm.
·40	20 secs.	35
·30	12	
·20	9	
·14	8¼	
·08	20?	
·04	11	
·02	11	

The change of velocity with the size is again shown.

The relative effects of the first four alcohols on the surface charge are shown in the curves here given. Curves are also given for comparison, showing the effect on the surface tension of the same four alcohols. These latter are taken

Fig. 1.

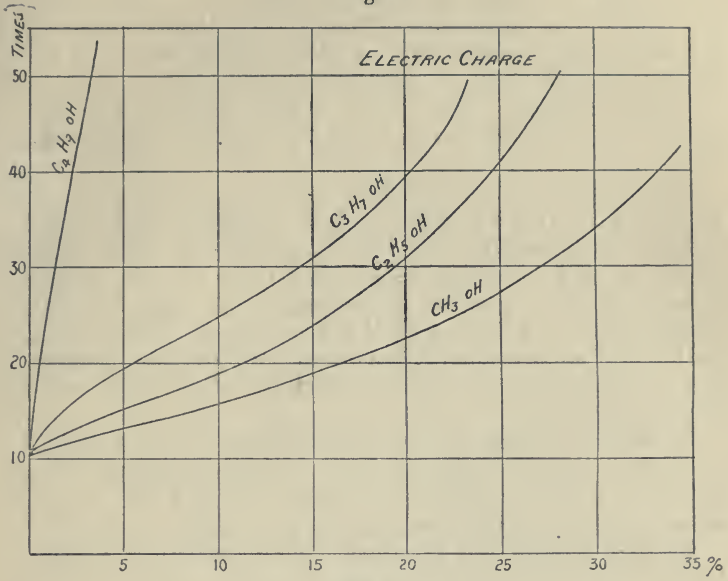
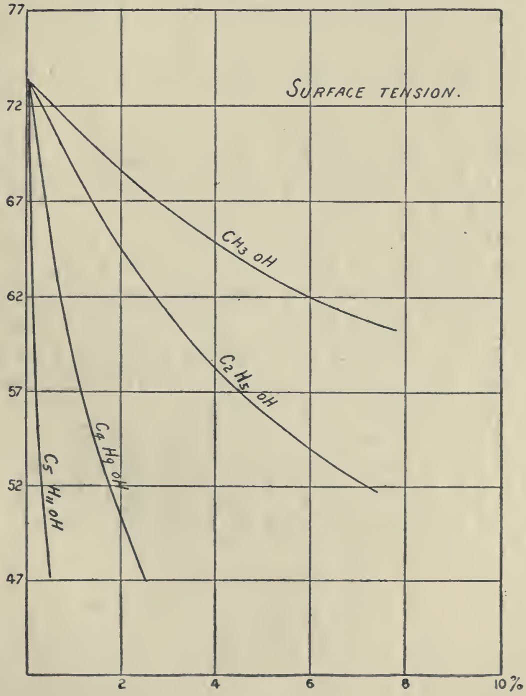

TIMES
ELECTRIC CHARGE
$C_4H_7 oH$
$C_3H_7 oH$
$C_2H_5 oH$
$CH_3 oH$
10
20
30
40
50
5
10
15
20
25
30
35 %

Fig. 2.


SURFACE TENSION.
$CH_3 oH$
$C_2H_5 oH$
$C_4H_9 oH$
$C_5H_{11} oH$
77
72
67
62
57
52
47
2
4
6
8
10 %

from Traube (*Journ. de Chim. et Phys.* iii. p. 587, 1905) and Freundlich (*Kapillarch.*, p. 64). The curves showing the effect of concentration on the velocity, *i. e.*, on the electric charge occur in the same order as in the case of surface tension. The alcohol which lowers the surface tension most rapidly also reduces the electric charge most quickly.

The pure alcohols themselves showed no cataphoresis of air-bubbles. This was not expected, particularly for methyl alcohol, because Baudouin (*C. R.* cxxxviii. pp. 898, 1165) found for it a small but easily measurable electric osmosis through certain porous diaphragms—the sign, however, depending on the nature of the diaphragm. Besides this, methyl and ethyl alcohols give rise to electrification in waterfall and in bubbling experiments, which might lead one to expect some effect.

In methyl alcohol, bubbles of air of a size ·10 mm. showed no sign of motion under potentials of 100 volts/cm. The application of the potential in this case had the curious effect of hastening the absorption of the bubble.

In ethyl alcohol 125 volts/cm. gave no motion to an air-bubble, not even in a 50 per cent. aqueous solution.

In a 25 per cent. solution of propyl alcohol no motion can be observed with 125 volts/cm. for air-bubbles artificially made.

In isobutyl alcohol no motion of an air-bubble is apparent.

It does not follow, of course, that a cataphoresis of other particles than air-bubbles does not occur in these alcohols, as the case of benzine spheres in 25 per cent. propyl alcohol shows as well as Baudouin's experiments.

The results for the first four fatty acids are given here. The concentrations are necessarily small for the reason explained in the last paper. A complete series of observations for formic acid is given to show again the effect of size, these acids being adsorbed like the alcohols and being very active in reducing the surface tension. The concentrations are given in ccs. of acid per c.c. of water.

The readings are not as regular as they should be—perhaps because of some unavoidable impurity introduced with the bubble by the pipette, or perhaps—where the final reading for a bubble is large—because of some residue left by the acid in the surface.

Formic acid and water.

Conc.	Diam.	Time.	Volts/cm.
10^{-6}	·16	22 secs.	35
	·10	16½	
	·06	15	
	·02	14	
10^{-6}. 1/2	·14	24	
	·10	16	
	·08	12½	
	·02	14	
10^{-6}. 1/4	·10	14	
	·08	13	
	·06	13	
	·02	15	
10^{-6}. 1/8	·12	13	
	·10	12½	
	·04	13	
10^{-6}. 1/16	·14	17	
	·10	13½	
	·06	14	
	·04	16½	
10^{-6}. 1/32	·14	18	
	·08	12	
	·06	12	
	·04	13½	
10^{-6}. 1/64	·14	14	
	·10	13½	
	·06	13½	
	·02	18	

Acetic acid and water.

Conc.	Diam.	Time.	Volts/cm.
10^{-4}	·12	23 secs.	35
10^{-4}. 1/4		28	
10^{-4}. 1/16		20	
10^{-4}. 1/64		14	
10^{-4}. 1/256		15	
10^{-4}. 1/1024		25	
10^{-4}. 1/4096		14	
Dist. water		11	

Propionic acid and water.

Conc.	Diam.	Time.	Volts/cm.
10^{-4}	·10	30 secs	35
$10^{-4}.1/2$		23	
$10^{-4}.1/4$		23	
$10^{-4}.1/8$		18	
$10^{-4}.1/16$		17	
$10^{-4}.1/32$		15	
$10^{-4}.1/64$		16	
$10^{-4}.1/128$		13	
$10^{-4}.1/256$		13	
Water		11	

Butyric acid and water.

Conc.	Diam.	Time.	Volts/cm.
10^{-6}	·14	22 secs.	40
$10^{-6}.2$	·12	40	
$10^{-6}.3$	·14	30	
$10^{-6}.4$	·12	50	
$10^{-6}.5$	·12	69	
$10^{-6}.6$	·12	33	
$10^{-6}.7$	·14	32	
$10^{-6}.8$	·14	32	
$10^{-6}.9$	·12	29	
10^{-5}	·12	30	

In the last table the solutions were each made separately and not by successive dilution as in the other cases.

On account of the difficulty of getting readings fairly consistent, only the most general comparison of the effects of these acids on the surface charge can be made. They all lower the charge as do inorganic acids, formic and butyric acting more vigorously than the others. They show parallel activity in lowering the surface tension. They exhibit with the alcohols the variation of charge with the size of the bubble.

Discussion.

The addition of alcohols to water reduces the electrification at the liquid-gas surface, the effectiveness of any alcohol corresponding in this respect to its effectiveness in reducing the surface tension of water. This reduction of surface tension is caused by a positive adsorption of alcohol into a surface layer of small thickness. In this layer there exists—on the electric double layer theory—a double layer of ions, the outer surface negative, the inner positive. The number of ions, *i. e.,* the charge, will be influenced by the relative proportions of alcohol and water in the layer. Consider a bubble of air in a mixture of alcohol and water. It is enclosed in a layer of small thickness which contains relatively more alcohol than the liquid around it. Suppose this surface to diminish in area by the gradual absorption of the air into the liquid. If, as the diameter of the sphere gets smaller and the curvature of the surface greater, the proportion of water in the surface layer increases, one would expect the electric charge to approach more nearly to the value it has in pure water—*i. e.*, one would expect a bubble to move faster under a given potential difference as it becomes smaller. This is exactly what happens in the case of the alcohols and other substances which exhibit a positive adsorption. It seems probable that this equalization of the concentration in the surface layer with that in the solution goes on as the bubble becomes smaller, until at the moment of disappearance the surface layer has the same concentration as the rest of the liquid. In other words, this effect indicates a dependence of the degree of adsorption upon the curvature of the surface—an effect analogous to the change of vapour pressure in pure liquids with the curvature of the surface.

An instance of an effect the converse of that shown by these organic substances was given in the last paper. In a solution of thorium nitrate a bubble of air decreased in velocity as it became smaller, and even reversed its direction of motion before disappearing. This behaviour is explained as before if the salt is negatively adsorbed—*i. e.*, if the surface layer at first contains less salt than the liquid.

It is rather unexpected to find that alcohol appears to show no electrical surface charge in these experiments, while in waterfall experiments or in bubbling experiments it does give a small electrification. Prof. Thomson (*loc. cit.*) in waterfall experiments found alcohol to give an effect, but much smaller than water. Bloch also (*Ann. de Chimie*, pp. 22 & 23, 1911) found it to be "active" in bubbling experiments. The difference in behaviour is probably due to the difference in the conditions of experiment. In cataphoresis experiments there is no violent mechanical rupture of the surface as in the other types of experiment. In waterfall experiments Lenard supposes this disturbance to tear apart the negative from the positive electrification in a double layer at the surface. If this is so, it cannot be the same double layer which surrounds a bubble of air and is active in a cataphoresis experiment. If it were, there should be parallel effects observed in the two cases. For example, Prof. J. J. Thomson has shown in waterfall experiments that the merest trace of methyl violet in the water reverses the electrification produced. The author has tried solutions of methyl violet in cataphoresis experiments, but found no reversal. Again, Prof. Thomson in his experiments showed that water falling through its own vapour gained no charge, and from similar results in other cases concluded that the liquid and the gas in contact must be chemically different to give any electrification. The author could not try a bubble of water vapour in water in a cataphoresis experiment, but found that particles of ice in water moved almost as fast as bubbles of air. In this case, at least, the two phases in contact need not be chemically different.

The mechanism which produces the electrification in waterfall experiments is different from that in cataphoresis experiments, and is most probably and most simply explained on Prof. Thomson's view mentioned in the last paper. Alcohol, in these cases, can unite with a molecule of oxygen for example, and when the combination is violently disturbed ionization may take place, while in a cataphoresis experiment an adsorption of the ions in the liquid is necessary. This may not be possible in alcohol.

Summary.

Alcohols reduce the electric charge at the liquid-air surface in water, showing in this respect a parallelism with their action on the surface tension of water.

There does not appear to be any cataphoresis of air bubbles in pure alcohols.

The fatty acids reduce the charge at the gas-liquid surface in aqueous solutions, but no reversal was observed with the concentrations used.

A large variation of velocity with size of air bubbles in cataphoresis experiments is produced by the presence in aqueous solution of substances which have a marked effect on surface tension.

Evidence is given to show that the electrification in waterfall experiments is not due to the difference of potential observed in the cataphoresis experiments.

From the PHILOSOPHICAL MAGAZINE, vol. xliv. *August* 1922.

On the Electrification at the Boundary between a Liquid and a Gas. By Professor H. A. McTAGGART, *M.A., University of Toronto* *.

MANY years ago, in the course of some experiments on the effect of an electric current on the motion of small particles in a liquid, Quincke (*Ann. d. Phys.* cxiii. p. 513, 1861) observed that small gas-bubbles in water moved as though negatively charged. Although a good deal of attention has been paid to the movement of solid and of liquid particles in such cases, very little effort has been devoted to the study of small spheres of gas suspended in a liquid—one obvious reason being the difficulty of controlling them while under observation. A systematic examination of their electrical properties ought, however, to yield further information as to the physics—and chemistry too—of surface layers.

Before the war experiments in this field were begun by the author in the Cavendish Laboratory under Sir J. J. Thomson, and some results were obtained. Measurements were made (Phil. Mag. Feb. 1914, p. 297) of the velocity, under a fall of potential, of small spheres of air in distilled water and their electrical charges were estimated. The effects on the charge of the addition of minute amounts of various inorganic electrolytes were studied. Results were obtained (Phil. Mag. Sept. 1914, p. 367) showing how the charge varies with the presence in the water of certain alcohols and organic acids, and a parallel was shown to exist between the variation of the electric charge and the surface tension.

The present paper deals with some further experiments carried out in the University of Toronto, and describes the variation observed in the electric charge on small spheres of air when a particular electrolyte, Thorium Nitrate [$Th(NO_3)_4$], was dissolved in water. This salt was selected for special study because it had been found to be unusually active in charging these surface layers.

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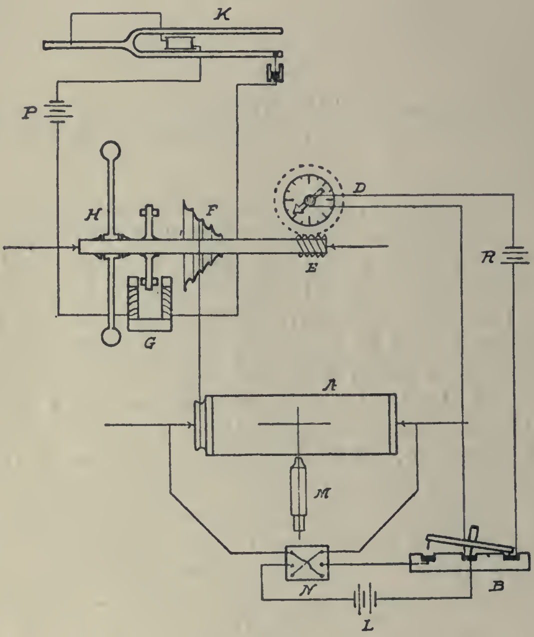
* Communicated by Professor J. C. McLennan, F.R.S.

The apparatus used was similar to that referred to in a former paper, one or two changes being made in it for greater convenience. The arrangement is shown in fig. 1.

Fig. 1.



A is a small cylindrical glass cell rotating about its axis on pivots and driven by a belt of thread from a pulley F on a Rayleigh motor. This motor was made in the laboratory workshop, and has, instead of the usual fly-wheel with a hollow rim filled with water, a solid brass wheel H—a modification suggested by Professor Wilberforce of Liverpool. The wheel, although loose on the shaft, has enough friction, when a heavy oil is used for lubricant, to keep the shaft in steady motion after synchronism with the tuning-fork is attained.

D is a timing device consisting of a vertical post carrying a pointer and made to rotate by a toothed wheel working in the worm E. The pointer rests by its own weight on the top of the post, but at any instant in its motion over the fixed dial D it may be raised and stopped by a small electromagnet controlled by the key B. When released it falls back on the post and begins to record time with the same regularity as the tuning-fork. It forms a very convenient stop-watch if velocities are to be measured.

A travelling microscope M measures the distance travelled by any bubble on the axis of the rotating cell.

The water used was twice distilled—the second time in "Pyrex" glass and condensed in a silver coil.

The thorium nitrate was by Merck, and was assumed to have 12 H_2O—water of crystallization.

A stock solution was made up containing 4×10^{-6} equivalents per c.c. (1/250 normal), and from this other solutions were made by successive dilution.

A first series of readings was taken with various concentrations of the salt, but with bubbles of nearly the same size in order to reproduce the effects previously observed—the method of working being to fill the cell A with the desired solution, introduce a single bubble of air with the gas pipette, and set the cell in rotation. The bubble very soon takes up a steady position on the axis, and its motion under any fall of potential L may be examined.

Very small concentrations sufficed to reduce to zero the natural negative charge found in pure water and to give the small sphere of air a positive charge.

The following readings are typical :—

Fall of potential .... 34 volts per cm.
Diameter of bubble...... 0·3 mm.

Concentration. Equivalents per c.c.	Sign of charge.	Velocity of bubble. cms./sec./volt./cm.
4×10^{-7}	+	5×10^{-4}
4×10^{-8}	+	slower
8×10^{-9}	+	very slow $(1{\cdot}5\times10^{-4})$
$5{\cdot}7\times10^{-9}$	–	slow
$4{\cdot}7\times10^{-9}$	–	faster
4×10^{-9}	–	faster
Pure water	–	4×10^{-4}

The zero point was reached at a concentration of about 7×10^{-9}, a result rather higher than that given in a former paper. The salt was an entirely different sample, and may not have contained the same proportion of water of crystallization. (See Abegg and Auerbach, ‘Inorganic Chemistry.’)

A series of readings was then taken for spheres of air of different sizes, one object being to observe the charge on very small spheres. It is very difficult, by the use of any kind of pipette, to introduce into the rotating cell bubbles smaller than 1/5 mm. in diameter. To avoid this difficulty the following mode of working was adopted. The solution was first placed in a partial vacuum to remove as much dissolved air as possible, and afterwards poured into the cell. A bubble into this gas-free solution slowly decreased in size by absorption until it vanished, while the electric charge could be observed at any stage.

Under these circumstances it was found that for a suitable concentration of solution a sphere of air which began with a small negative charge almost invariably and in a regular way reduced its charge to zero, and gradually took on a positive charge.

The following readings illustrate this point —

No. 1.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5{\cdot}7$	0·26	–
	0·17	–
	0·14	–
	0·10	0
	0·08	+

No. 2.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5{\cdot}7$	0·44	–
	0·35	–
	0·26	–
	0·17	0
	0·14	+

No. 3.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5{\cdot}7$	0·62	—
	0·53	—
	0·39	+
	0·17	+
	0·08	+

No. 4.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5{\cdot}7$	0·71	—
	0·53	—
	0·44	—
	0·35	0
	0·32	+
	0·23	+

No. 5.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5{\cdot}7$	0·28	—
	0·17	—
	0·08	—
	0·05	—

It will be seen from the first four examples given that at a concentration of $10^{-9} \times 5{\cdot}7$ the change of sign occurs in every case. Rarely, as in No. 5, and then only when the original sphere was small, did the sign remain the same. Even then the charge grew steadily less. In practically every case the negative charge slowly decreases as the bubble gets smaller, passes through zero, and increases to a small positive value.

Three examples are given for slightly greater concentrations :—

No. 6.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9}\times 6{\cdot}6$	0·53	–
	0·41	0
	0·35	+
	0·17	+
	0·08	+

No. 7.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9}\times 6{\cdot}6$	0·35	–
	0·28	0
	0·26	+
	0·17	+
	0·14	+

No. 8.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9}\times 8$	0·44	Almost zero.
	0·35	+
	0·17	+

Above a concentration of $10^{-9}\times 8$ the bubbles were always positive.

The examples given show that the spheres do not all have the same size when they reach the zero—isoelectric—point in a given solution. The larger a sphere is at the beginning the larger it is when its charge becomes zero. This suggests, as the cause of the change in sign, a kind of coagulation of something in the free surface.

It is known that, in a solution of thorium nitrate in water, hydrolysis occurs with the formation of thorium hydroxide thus—

$$Th(NO_3)_4 + 4\ HOH \rightarrow Th(OH)_4 + 4\ HNO_3.$$

There is present in the solution some of the original salt, some acid, and the hydroxide in colloidal form. The presence of the last-mentioned was suspected as one of the causes producing the reversal of sign, and experiments were then made to test its activity in altering the charge.

A colloidal solution of thorium hydroxide as free as possible from salt and acid was prepared by dialysis (Burton, 'Physical Properties of Colloidal Solutions,' 2nd Ed., p. 16). A dialysing "sleeve" shaped in the form of a test-tube was made of "parlodion" (sold by the Du Pont Chemical Co., New York). A solution of the parlodion in ether and alcohol was used to coat the inside of a test-tube of suitable size. After the solvent had evaporated the parlodion remained as a thin but strong film which when detached from the glass served very well as a dialysing vessel.

For this experiment a solution containing about 2 gm. of salt in 50 c.c. of water was dialysed for a period of three weeks, after which an estimate was made of the colloid present. A sample of 10 c.c. evaporated over sulphuric acid gave a residue of ·0034 gm. The residue formed a thin layer of gelatinous material on the bottom of the evaporating dish, with drying cracks across it in all directions.

The effect of this colloid on the charge on small spheres of air in water was then examined, the dialysed solution above mentioned being diluted as shown in the following examples:—

No.	C.c. colloid solution in 100 c.c. water.	Diameter of sphere in mm.	Sign of charge.
1	10	0·21	+
		0·12	+
		0·07	+
2	5	0·17	+
3	2·5	0·17	+
		0·07	+

It is seen that the surface is charged positively by the presence of very small amounts of the colloid.

The following examples show the gradual reversal of the sign of the charge accompanying the absorption of the bubble :—

No.	C.c. colloidal solution in 100 c.c. water.	Diameter of sphere in mm.	Sign of charge.
4	1·0	0·17	–
		0·14	+
5	0·5	0·35	–
		0·26	–
		0·12	+
		0·05	+
6	0·25	0·32	–
		0·17	–
		0·08	–
		0·05	+

The experiments show that the colloidal thorium hydroxide gives both the effects observed with the ordinary solution. It not only charges the surface positively if present in sufficient amount, but it also exhibits the reversal of charge with diminishing size of the bubble, and this, too, in concentrations of thorium of about the same order as in the case of the salt.

Discussion.

The state of the matter and the nature of the electric forces in surface layers of liquids is still a subject on which no very clear ideas exist. Experiments on electro-endosmosis all point to a selective action in such layers so far as the ions in the solution are concerned. But the observations are always complicated by the presence in contact with the liquid surface of a solid whose role in the selecting we are ignorant of. The same is true of cataphoresis experiments with solids, as, for example, in the study of the electrical charge on colloidal particles. This difficulty is avoided, however, in similar experiments with small spheres of air—or any gas—and in such cases we can safely regard any effects observed as due largely to the properties of the liquid and its free surface. In particular, the electrical charge existing at any air-liquid surface may be considered as the result of forces residing altogether in the liquid. It ought to be possible, then, in considering potential differences at solid-liquid junctions to isolate the contribution of the liquid.

In the case of thorium nitrate in solution the selective action of the air-water surface is very marked, a positive charge being acquired by the surface with very minute concentrations of the salt. The positive ions available for selection are Th^+ and H^+, but neither of these separately can be responsible for the unusual activity of the salt. The mere presence of H^+ ions, as, for example, in the form of an acid, does not produce so great an influence on the surface charge. Nor can free Th^+ ions have much effect, for they disappear in the dialysis and yet leave the pure colloidal solution practically as active as before. The real agent must be the particles of colloidal thorium hydroxide which gather about them groups of H^+ ions and carry them into the surface in larger numbers than would be possible for the H^+ ions alone.

The nature of this selective action must be connected with the shape of the surface, or, to put it in another way, a particle must reach a certain size before it can be regarded as having a surface-layer about it with a tension and an electric charge. We have at present in order of size—ions, ionic micelles (Prof. McBain, "Soap Solutions," Nature, March 10, 1921), ultra-microscopic colloidal particles, microscopic and macroscopic particles including gas-bubbles. At what stage a surface-layer is formed it is difficult to say, but it seems reasonable to suppose that the curvature of such a surface would have an effect on the charge adsorbed. The change of sign with decreasing size of air-sphere shown in these experiments seems to bear out this idea.

The information obtained regarding the effect of thorium nitrate on the electrification of air-water surface layers may be summarized as follows :—

1. Thorium nitrate in aqueous solution and in concentrations as small as 8×10^{-6} normal gives a positive electric charge to the surface of a sphere of air immersed in it. (In distilled water the charge is always negative.)

2. For concentrations in the neighbourhood of 6×10^{-6} normal a sphere initially negative becomes gradually positive as the sphere diminishes in size.

3. Colloidal thorium hydroxide in small concentrations of the same order also gives a positive electric charge to a sphere of air immersed in it.

4. Colloidal thorium hydroxide also exhibits the reversal of the sign of the charge with a decrease in the size of the bubble.

5. It is suggested that this reversal of sign is experimental evidence of a relation between the curvature of the surface and its adsorptive power.

The experiments are being continued as time permits in the hope of obtaining some new information regarding these free surfaces. Is is the intention to compare with thorium the effects of one or two other tetravalent and trivalent metals in the colloidal state.

I wish to thank Professor J. C. McLennan for his kind and encouraging interest in the work.

Physics
Elect
M

Author McTaggart, Henry Allen

Title On the electrification at the boundary between a liquid and a gas.

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